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(54) Title: ELASTOMERIC COPOLYMER OF ETHYLENE WITH α -OLEFINS			
(57) Abstract			
<p>Copolymers of ethylene with propylene and/or higher α-olefins and, optionally, minor proportions of a diene or polyene, which display the following properties: crystallinity content, measured as fusion enthalpy, lower than 20 J/g; solubility in pentane at 25 °C higher than 90%; content of propylenic units or units deriving from said α-olefins in the form of triads comprised between 4 and 50% of the total content of propylene or said α-olefins, with at least 70% of said triads having an isotactic structure; product of the monomer reactivity ratios $r_1.r_2$ comprised between 0.4 and 1; inherent viscosity higher than 1.5 dl/g.</p>			

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ELASTOMERIC COPOLYMER OF ETHYLENE WITH α -OLEFINS

The present invention relates to new copolymers of ethylene with propylene and/or higher α -olefins, optionally containing minor amounts of units deriving from a diene or polyene, showing valuable elasto-plastic properties also in a non-cured state.

EP and EPDM rubber, which respectively are elastomeric copolymers of ethylene with propylene and with minor proportions of a diene or polyene, are well known products in the art.

Such copolymers are generally prepared by polymerization of mixtures of ethylene and propylene and optionally of a diene or polyene with Ziegler-Natta catalysts obtained from vanadium compounds, such as vanadium acetylacetone and alkyl-Al halides.

The resulting copolymers require a vulcanization treatment (with peroxides or sulphur) in order to be able to acquire an elastomeric behaviour of interest.

Thermoplastic polyolefin rubbers (TPO) are known which are capable of retaining the processability characteristics of thermoplastic polymers and simultaneously displaying an elastomeric behaviour. These rubbers are obtained by means of high-temperature dynamic vulcanization, in the presence of crosslinking agents, of blends of crystalline polyolefins, in particular isotactic polypropylene, with EP or EPDM rubbers.

Copolymers endowed with a certain level of elasto-plastic properties are known; they are obtained by polymerization of propylene mixtures with minor proportions of ethylene, using catalyst based on titanium compounds supported on magnesium

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chloride (US Patent 4,298,721). These copolymers are characterized by a large content of crystallinity of polypropylenic type, and optionally of polyethylenic type; the elastomeric properties of these copolymers are unsatisfactory (200% tension set values are too high).

Preparing elastomeric copolymers of ethylene with propylene and/or with α -olefins and optionally with minor proportion of a diene or polyene by means of the polymerization of mixtures of monomers with homogeneous catalysts obtained from Ti, Zr or Hf metallocenes and alumoxane compounds, is known.

European Patent Application EP-A-347128 describes a process for the preparation of elastomeric copolymers of ethylene with α -olefins in which the catalyst used is the product obtained from the reaction of dicyclopentadienyl-Zr, -Ti or Hf compounds, such as ethylene-bis(indenyl)-zirconium dichloride or ethylene-bis(tetrahydroindenyl)-zirconium dichloride or dimethylsilanylene-bis(tetrahydroindenyl)-zirconium dichloride, with polymethylalumoxane. Catalysts promoting the isospecific polymerization of α -olefins and non-stereospecific catalysts are indifferently used. The polymerization is carried out in liquid monomer at temperatures comprised between 0 and 80 °C, preferably between 20 and 60 °C.

European Patent Application EP-A-347129 describes a process for the preparation of elastomeric copolymers of ethylene with α -olefins containing minor proportions of a non-conjugated diene,

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analogous to the one disclosed in European Patent Application EP-A-347128.

None of the copolymers disclosed in both the above cited EP applications or in the examples shows satisfactory elasto-plastic properties in the non-vulcanized state. 200% tension set values are higher than 30% and the tensile strength is lower than 4-5 MPa.

European Patent Application EP-A-374,695 describes propylene copolymers with ethylene, in which propylene is present in amounts higher than about 57% by mol, containing isotactic polypropylenic sequences obtained by the polymerization of said olefins with catalysts prepared from bridged metallocenes, such as ethylene-bis(tetrahydroindenyl)-zirconium dichloride and polymethylalumoxane. The polymerization is carried out at low temperature, approximately 0 °C in the examples. The copolymers do not display any elasto-plastic properties of interest.

Up to now, no copolymers of ethylene with propylene and/or α-olefins, optionally containing units deriving from dienes or polyenes, are known which display in their uncured state elastoplastic properties of interest (200% tension set values, 1 min, 25 °C, lower than 30%; tensile strength higher than 3-4 MPa).

It has now been unexpectedly found that copolymer having the above indicated elasto-plastic properties can be synthesised.

The copolymers have an ethylene content comprised between 45 and 85 % by mol, preferably between 50 and 75 % by mol, a content

of propylene and/or α -olefins $\text{CH}_2=\text{CHR}$, in which R is a $\text{C}_2\text{-}\text{C}_{10}$ alkyl radical, comprised between 15 and 55 % by mol, preferably between 25 and 55 % by mol, and a content of diene or polyene comprised between 0 and 10 % by mol.

The copolymers are characterized by:

- solubility in pentane at 25 °C higher than 90%;
- substantial absence of crystallinity (fusion enthalpy lower than 20 J/g);
- content of propylene units, or units deriving from said α -olefin, as triads comprised between 4 and 50% of propylene or of said α -olefin; at least 70% of said triads display an isotactic structure;
- a random distribution of ethylene units and propylene units and/or units deriving from said α -olefins in the portion of chain having copolymeric structure (values of the product of the comonomer reactivity ratios comprised between 0.4 and 1).

The high elasto-plastic properties of said copolymers are evidenced by the low values of tension set at 200%, 1 min, 25 °C (the values are generally comprised between 10 and 20%) and by the high tensile strength, higher than 4 MPa and generally comprised between 5 and 7 MPa.

When under stretch (stretch ratio = 4:1), the copolymers display, in their X-ray diffraction fibre spectra, signals which may be attributed to a partial orientation or crystallization of the macromolecular chain.

The copolymers have an inherent viscosity higher than 1.5 dl/g and generally comprised between 2.5 and 3.5 dl/g.

The solubility in pentane is preferably higher than 95%.

The content of diene or polyene units is generally comprised between 0 and 10 % by mol, preferably between 0.5 and 5 % by mol.

The copolymers can be transformed into shaped articles by means of the normal processes of manufacturing of thermoplastic materials (compression moulding, extrusion, injection moulding, etc.) and the resulting articles display elastic properties comparable to those of vulcanized rubbers.

If so desired, the copolymers can be vulcanized by using the same formulations and methodologies as known for EP and EPDM rubbers; rubbers endowed with valuable elastomeric properties are obtained.

The copolymers of the present invention are prepared by polymerization of mixtures of ethylene with propylene and/or with a α -olefin $\text{CH}_2=\text{CHR}$, in which R is an alkyl radical having 2-10 carbon atoms, optionally in the presence of a diene or a polyene, with chiral catalysts obtained from metallocene zirconium derivatives, ethylene-bis(tetrahydroindenyl)-zirconium dichloride or dimethylsilanylene-bis(tetrahydroindenyl)-zirconium dichloride and tetraisobutylalumoxane.

Further α -olefins which may be used beside propylene are, for instance, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-dodecene. The dienes or polyenes which can be used are preferably selected from linear non-conjugated diolefins,

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such as 1,4-hexadiene, or internal-bridged cyclic diolefins, such as 5-ethylidene-2-norbornene.

The copolymerization is carried out in the liquid phase constituted by propylene and/or by said α -olefin, operating at a temperature of approximately 40-50 °C.

Characterizations

The thermal behaviour of the polymer was analyzed on a polymer sample as polymerized, by means of differential scanning calorimetry, according to the following procedure: first scanning stroke from $T_1=-20$ °C to $T_2=180$ °C, with a heating rate of 20 °C/minute; solidification at the cooling rate of 20 °C/minute and a second scanning stroke with the same modalities as of the first one. The reported data of fusion enthalpy refer to the first scanning stroke.

The content of bound ethylene was determined by means of infrared analysis.

The content of propylenic triads or of triads of units derived from the other α -olefin was determined by means of ^{13}C -NMR, with reference to the methine $T_{\beta\beta}$, as already reported in "G.J. Ray, P.E. Johnson, J.R. Knox, Macromolecules, 10, 4, 773 (1977)". The reported numeric values refer to the content of propylene or of the other α -olefin.

The content of isotactic triads was determined by means of ^{13}C -NMR, by applying the following formula:

$$\text{Iso\%} = (A[T_{\beta\beta}]_{mm}) / (A[T_{\beta\beta}]_{mm} + A[T_{\beta\beta}]_{mr} + A[T_{\beta\beta}]_{rr}),$$

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wherein A is the area subtended under the peaks relevant to tertiary carbon atoms ($T_{\beta\beta}$); mm, mr and rr respectively are the isotactic, heterotactic and syndiotactic triads.

The product of the reactivity ratios $r_1 \cdot r_2$ (r_1 is the reactivity ratio of ethylene, r_2 of the other olefin) was calculated by means of the following formula:

$$r_1 \cdot r_2 = 1 + f \cdot (x+1) - (f+1) \cdot (x+1)^{1/2},$$

in which

f = (ethylene mols/propylene mols)_{copolymer};

x = ration between the percentage of propylene in two or more consecutive units and percentage of isolated propylene.

The values of tension set and tensile strength were measured according to ASTM D412.

The solubility in pentane was determined as follows: 2 g of polymer was placed in 250 ml of n-pentane; the latter was heated to boiling temperature, whilst stirring, for 20 minutes and was left to cool down to 25 °C whilst stirring. After 30 minutes the resulting mixtures was filtered through a pleated filter; after vacuum drying the portion of insoluble polymer was determined.

The following examples are supplied for illustrative purposes and shall not be construed as being limitative of the invention.

EXAMPLES

Preparation of the catalytic system

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Ethylene-bis(tetrahydroindenyl)-zirconium dichloride (EBTHIZrCl₂) was prepared by following the method described in H.H.Britzinger et al., J.Organomet.Chem., 288, p.63, (1985).

Tetraisobutylalumoxane (TIBAO) was prepared according to the Example 2 reported in EP-A-384171.

To a weighed amount of EBTHIZrCl₂, toluene was added at a volume rate of 2 ml per each mg of metallocene. To such a solution, a toluenic solution of TIBAO was added in such an amount as to obtain the values of Al/Zr ratio and of the molar Al concentration as reported in Table 1. The reaction mixture was kept stirred at the temperature and for the time period reported in Table 1.

General Polymerization Procedure

A 4 litre steel autoclave equipped with a stirrer, pressure gauge, thermometer, catalyst loading system, monomer feeding lines and thermostatting jacket, was used. 2 litres of propylene, hydrogen until a concentration thereof of 0.1% by mol was reached in the gas phase in the end mixture and ethylene up to the desired pressure at 50 °C, were charged to the autoclave, previously purged with propylene; the toluenic solution containing the catalytic system, prepared according to the above reported modalities, was injected.

The polymerization was carried out at 50 °C, with the total pressure kept constant by feeding ethylene. The polymerization conditions are reported in Table 1. At the end of the

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polymerization, the polymer was recovered by removing any unreacted monomers and is dried under vacuum.

EXAMPLE 1-7

By following the above reported general methodology, some polymerization tests were carried out, under such operating conditions as reported in table 1.

In Table 2 , the characterization of the resulting polymer is reported.

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TABLE 1

Example No.	Zr (mmol \cdot 10 $^{-3}$)	TIBAO (Al mmol)	Al/Zr (molar ratio)	Al (mmol/l)	Catalyst preparation		
					Al (M)	T (°C)	t (min)
1	4.69	8.5	2026	3.6	0.8	20	20
2	4.69	8.5	2026	3.6	0.8	40	20
3	1.17	4.76	4088	1.8	0.6	20	20
4	4.69	8.5	2026	3.61	0.20	20	60
5	4.69	8.5	2026	3.6	0.81	20	8
6	9.38	19.0	2026	7.2	1.80	20	8
7*	11.72	8.5	810	3.58	0.51	20	10
						 (cont.)

* Terpolymerization carried out with ethylidene-norbornene: 0.87% by weight in the polymerization mixture;

21.1 g is gradually fed during the course of the polymerization.

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TABLE 1 (cont.)

Polymerization					
C ₂ in liquid phase (wt%)	C ₂ pressure (bar)	H ₂ /gas (mol %)	P tot. (bar)	t (min)	Yield (g)
18	16.2	0.1	34.8	240	641
18	16.2	0.1	34.8	240	263
18	16.2	0.1	34.8	120	190
18	16.2	...	34.8	240	400
18	16.2	0.1	34.8	240	342
18	16.2	0.1	34.8	240	760
17.8	16.2	0.1	34.8	300	620

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TABLE 2

Example No.	% C ₂ (by wt.)	I.V. (dL/g)	M _w /M _n	DSC		DSC	
				I scan.	H _i	II scan.	H _i
1	66.7	2.78	3.1	37.8	0.7
2	66.4	3.63		42.3	3.9	36.3	3.8
3	62.6	2.63		17.8	1.0	38.4	6.4
4	69.6	4.24		47.0	8.2
5	64.4	2.3		40.6	11.9
6	61.2	2.4		43.3	9.93
7*	66.3	3.1	1.83	44.8	1.6	37.0	0.6

* Terpolymer with ethylen-norbornene.

... (cont..)

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TABLE 2 (cont.)

NMR analysis			Solubility (weight %)		Tension Set (%)	Tensile Strength (MPa)
triads (%)	Iso %	$r_1 \cdot r_2$	soluble fraction	insoluble fraction		
20	100	0.80	100	--	14	6.2
			100	--	18	7.57
			100	--	18	7.08
			100	--		
12.3	100	0.876	100	--	40	
18.6	100	0.878	100	--	36	
16.4	86	0.89	100	--	22	0.1

SUBSTITUTE SHEET

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CLAIMS

1. Copolymers of ethylene with propylene and/or with α -olefins $\text{CH}_2=\text{CHR}$, in which R is $\text{C}_2\text{-C}_{10}$ alkyl radical, and optionally with minor proportions of units deriving from a diene or a polyene, containing from 45 to 85% by mol of ethylene, from 15 to 55% by mol of propylene and/or α -olefin, and from 0 to 10% by mol of diene or polyene, characterized by the following properties:
 - crystallinity content, as measured as fusion enthalpy, lower than 20 J/g;
 - solubility in pentane at 25 °C higher than 90%;
 - content of propylenic units or units deriving from said α -olefin, in the form of triads comprised between 4 and 50% of the total content of propylene or said α -olefin; at least 70% of said triads displaying an isotactic structure;
 - product of monomer reactivity ratio $r_1 \cdot r_2$, comprised between 0.4 and 1 (r_1 is the reactivity ratio of ethylene, r_2 is the reactivity ratio of propylene or said α -olefin);
 - inherent viscosity higher than 1.5 dl/g.
2. Copolymers according to claim 1, characterized in that the content of ethylene is comprised between 50 and 75% by mol, the content of propylene and/or said α -olefin is comprised between 25 and 50% by mol and the content of said diene or polyene is from 0 to 2% by mol.
3. Copolymers of ethylene and propylene according to claim 2, containing from 0 to 2% by mol of units deriving from a non-

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conjugated diene having a linear structure or a bridged cyclic structure, characterized by the following properties:

- product of monomer reactivity ratios r_1, r_2 , comprised between 0.5 and 0.9;
- propylene content in the form of triads comprised between 10 and 35% of the total content of propylene in the copolymer, with at least 70% of said triads having an isotactic structure;
- inherent viscosity higher than 2 dl/g;
- solubility in pentane higher than 95%.

4. Copolymers according to claim 3 characterized in that said non-conjugated diene is selected from 1,4-hexadiene and 5-ethylidene-2-norbornene.
5. Copolymers according to any of claims 3 or 4, characterized in that they display when stretched (stretching ratio = 4 : 1), X-ray diffraction fibre spectra containing signals due to partial orientation or crystallization of the macromolecular chains.
6. Copolymers according to any of claims from 1 to 5, characterized by a tension set (200%, 20 °C, 1 minute) lower than 30% and a tensile strength higher than 4 MPa.
7. Copolymers according to any of claims from 1 to 6, vulcanized with peroxides or sulphur.
8. Manufactured articles obtained from the copolymers according to any of claims from 1 to 7.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 93/00698

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F210/16; C08F210/18

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	C08F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB,A,2 053 246 (NAPHTACHIMIE) 4 February 1981 see claims 1-3; examples 2,3 see comparative examples C1 , C2 ---	1
A	EP,A,0 243 127 (BP CHEMICALS) 28 October 1987 see claim 1; example 1 ---	
A	EP,A,0 275 925 (SUMITOMO CHEMICAL COMPANY) 27 July 1988 see claim 1; examples 1,2 see comparative example 2 ---	1
A	MAKROMOL. CHEM. vol. 191, no. 12, December 1990, BASEL pages 2853 - 2864 , XP205133 'Effect of catalyst isospecificity on olefin copolymerization' -----	

¹⁰ Special categories of cited documents :¹⁰^{"A"} document defining the general state of the art which is not considered to be of particular relevance^{"E"} earlier document but published on or after the international filing date^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)^{"O"} document referring to an oral disclosure, use, exhibition or other means^{"P"} document published prior to the international filing date but later than the priority date claimed^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"A"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 08 JULY 1993	Date of Mailing of this International Search Report 26.07.93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer FISCHER B.R.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

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SA 72050

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-2053246	04-02-81	FR-A-	2460964	30-01-81
		BE-A-	884179	05-01-81
		CA-A-	1146699	17-05-83
		DE-A, C	3025398	08-01-81
		JP-C-	1310641	11-04-86
		JP-A-	56014509	12-02-81
		JP-B-	60034962	12-08-85
		LU-A-	82578	08-10-80
		NL-A-	8003827	08-01-81
		US-A-	4677172	30-06-87
EP-A-0243127	28-10-87	FR-A-	2597487	23-10-87
		CA-A-	1268298	24-04-90
		DE-A-	3772430	02-10-91
		US-A-	4797461	10-01-89
EP-A-0275925	27-07-88	JP-A-	63178113	22-07-88
		JP-A-	63202641	22-08-88
		JP-A-	63245451	12-10-88
		JP-A-	63273656	10-11-88
		JP-A-	1075552	22-03-89
		US-A-	5118773	02-06-92
		US-A-	5179156	12-01-93